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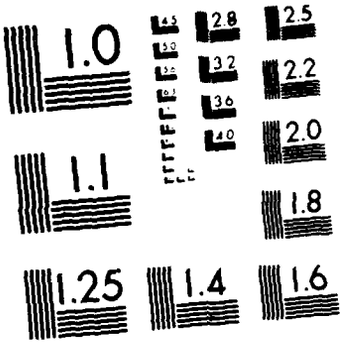

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ABSTRACT (Continue on reverse if necessary and identify by block number)

A disposable, 70 microliter, liquid-analysis transmission cell is described for use in near-infrared reflectance instruments. The small sample volume relative to the overall cell size allows many analyses to be performed without a thermostatically controlled heating cycle. Complex purge/fill and wash cycles are also unnecessary. The cell is ideally suited for the analysis of potentially hazardous liquid samples.

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TECHNICAL REPORT NO. 22

A DISPOSABLE LIQUID MICROCELL FOR NEAR-INFRARED REFLECTANCE ANALYSIS

by

Robert A. Lodder and Gary M. Hieftje

Prepared for Publication

in

APPLIED SPECTROSCOPY

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Bloomington, Indiana 47405

22 February 1988

While near-infrared reflectance instruments are best known for their ability to rapidly analyze powdered solid samples[1-2], some manufacturers have provided the means to measure liquid samples as well. Unfortunately, liquid-analysis accessories are often cumbersome and expensive. A typical accessory requires a relatively large volume of the sample (on the order of milliliters) and complex purge/fill and wash cycles to prevent clogging. If clogging does occur, cleaning can be difficult. The thermostatically controlled heating cycle only adds to a total analysis time already extended by the other operations.

Figure 1 depicts an alternative liquid cell and cell holder for the Technicon InfraAlyzer 400, constructed from solid aluminum and a single-cavity microscope slide with a cover slip. The main body of the cell holder has machined into it a 90 degree conical reflector and is based on a design used to analyze intact pharmaceutical capsules[3]. This main body fits into the solid-sample drawer of the spectrometer in place of the standard closed sample cup. The reflector is a polished curved surface of a right-circular cone with a height and a base radius of 13 mm. A hole 2 mm in diameter located at the vertex of this cone serves to stabilize a polished aluminum insert. This insert is essentially a cylinder capped with a second right-circular cone whose base is oriented in the direction opposite to that of the main body cone. The cone on the insert is machined with a vertex of 135 degrees. A standard single-cavity

microscope slide (25 x 76 mm) is centered with its 22 x 22 mm cover slip over the insert. The position of the slide is made stable and reproducible by resting it against two screws fastened into the main body.

The cavity slide has some distinct advantages over a conventional flat microscope slide in this application: (1) it provides a longer and more reproducible optical pathlength, (2) the cover slip acts as a lid on the cavity and lowers the liquid-sample evaporation rate, and (3) the cavity shape acts as a lens to scatter transmitted light into the integrating sphere of the spectrophotometer. A fully filled liquid cell based on a single-cavity slide (Dickinson and Company, Parsippany, NJ, #3720) and an ordinary cover slip (American Scientific Products, McGaw Park, IL, #M6045-2) contains 110 microliters of sample. However, different slides and cover slips with different masses can be used to vary the optical pathlength and the sample cell volume. The cover slip actually floats on the sample, and heavier cover slips tend to squeeze the sample and reduce the cell volume. When the cover slip is resting against the slide the cell volume is 70 microliters.

The 135-degree aluminum insert returns collimated light that passes through the slide back through the slide parallel to the walls of the main-body reflector cone. This design allows the bulk of the light that passes through the liquid in the cavity to be reflected directly into the instrument's integrating sphere at a 45 degree angle from the source light.

In this design the 135-degree conical portion of the insert is placed atop a small cylinder because the sample is actually below the integrating sphere; if the insert cone were to be lowered to the bottom (vertex end) of the main-body reflector cone much of the reflected light would miss the window of the integrating sphere.

Initial tests of this liquid cell included an analysis of a set of aqueous sodium chloride solutions. The determination of sodium chloride in water can be difficult for several reasons[4], including: (1) sodium chloride has no absorption bands in the near-infrared, (2) water has very strong absorption bands in the near-infrared, and (3) these water absorption bands are very temperature-dependent. Nevertheless, successful determinations of aqueous sodium chloride in concentrations from 30-38 grams per liter have been reported[4] by using four wavelengths selected in a standard multiple linear regression procedure.

Twenty aqueous solutions of reagent-grade sodium chloride (ten for the training set and ten for the validation set) were prepared for analysis in the new liquid cell. Solutions ranged in concentration from 5 to 38 grams per liter. Each solution was loaded into a single-cavity slide two times, and four spectra were taken from each sample loading. Spectra were recorded at 16 wavelengths and the data were transformed to their principal axes to avoid the need for a time-consuming all-possible-combinations of wavelengths regression. In order to

demonstrate that one need not be very particular about the initial selection of analytical wavelengths, the wavelength data near water absorption peaks were deliberately deleted from the recorded spectra (which contained data from 19 wavelengths). This also shows that relatively complex instruments, utilizing scanning monochromators to collect data at hundreds of wavelengths, are often unnecessary in NIRA.

Multiple linear regression was then carried out on the 80 training spectra using only the data along the first five principal axes (these axes accounted for over 99.9% of the total spectral variation). Data from five axes (rather than the four used in reference 4) were required because evaporative loss from the cell produced pathlength variations that called for an additional degree of freedom in the system. The results of the training process are summarized in the calibration line in Figure 2. The r^2 for the training set that produced the line is 0.97, and the r^2 value for the 80 validation spectra (shown superimposed on the calibration line, with error bars) is also 0.97. The detection limit for sodium chloride, calculated from both the error in the validation spectra and from four solvent blanks, is 1 gram per liter (1000 ppm). This value corresponds to an absolute detection limit of approximately 100 micrograms in the 110 microliter sample cell.

The liquid microcell that has been described here has a number of practical advantages. It is faster and easier to use than an ordinary liquid accessory. No heating or thermostatting

is required because 110 microliters of liquid rapidly reaches thermal equilibrium. No purging/filling or wash cycles are required. Any number of cells can be rapidly filled with a precision pipette if desired, and the cells can be easily cleaned or simply discarded afterward (an advantage for potentially dangerous and toxic samples). The configuration of the cell permits sensitive detection by enhancing transmission through the sample in a reflectance instrument. The apparent lack of pathlength reproducibility for volatile samples is compensated simply by using a random selection of pathlengths when the training-set spectra are recorded and by letting the calibration process take care of the rest. This microcell design adds a versatility to liquid analysis in near-infrared reflectance instruments that complements the flexibility of the near-infrared calibration procedure.

ACKNOWLEDGEMENTS

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2. D. L. Wetzel, *Anal.Chem.* **55**(12), 1165A (1983).

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FIGURE CAPTIONS

Figure 1. A cross-section of the microsample cell.

Figure 2. NIR calibration for NaCl in H_2O, obtained with the new microcell.

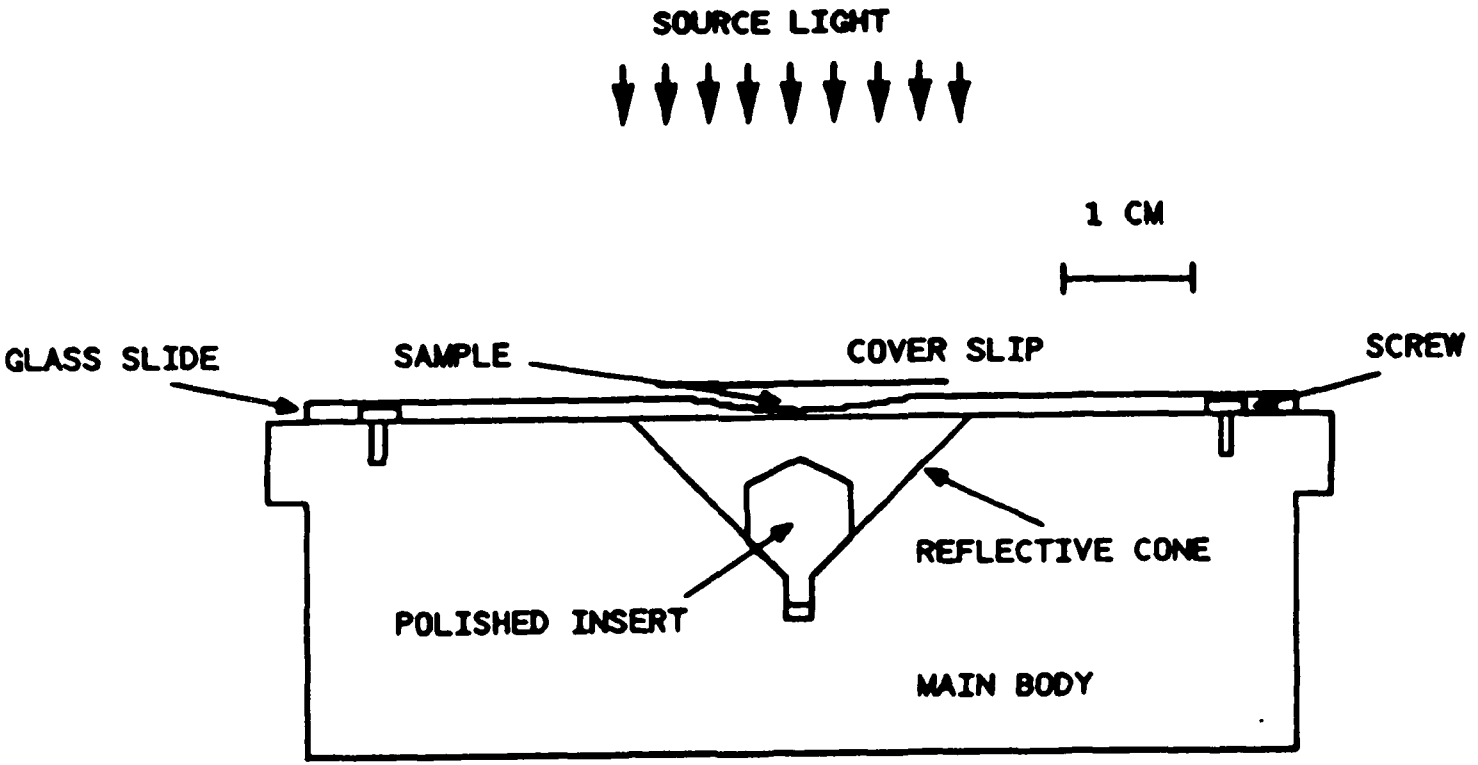
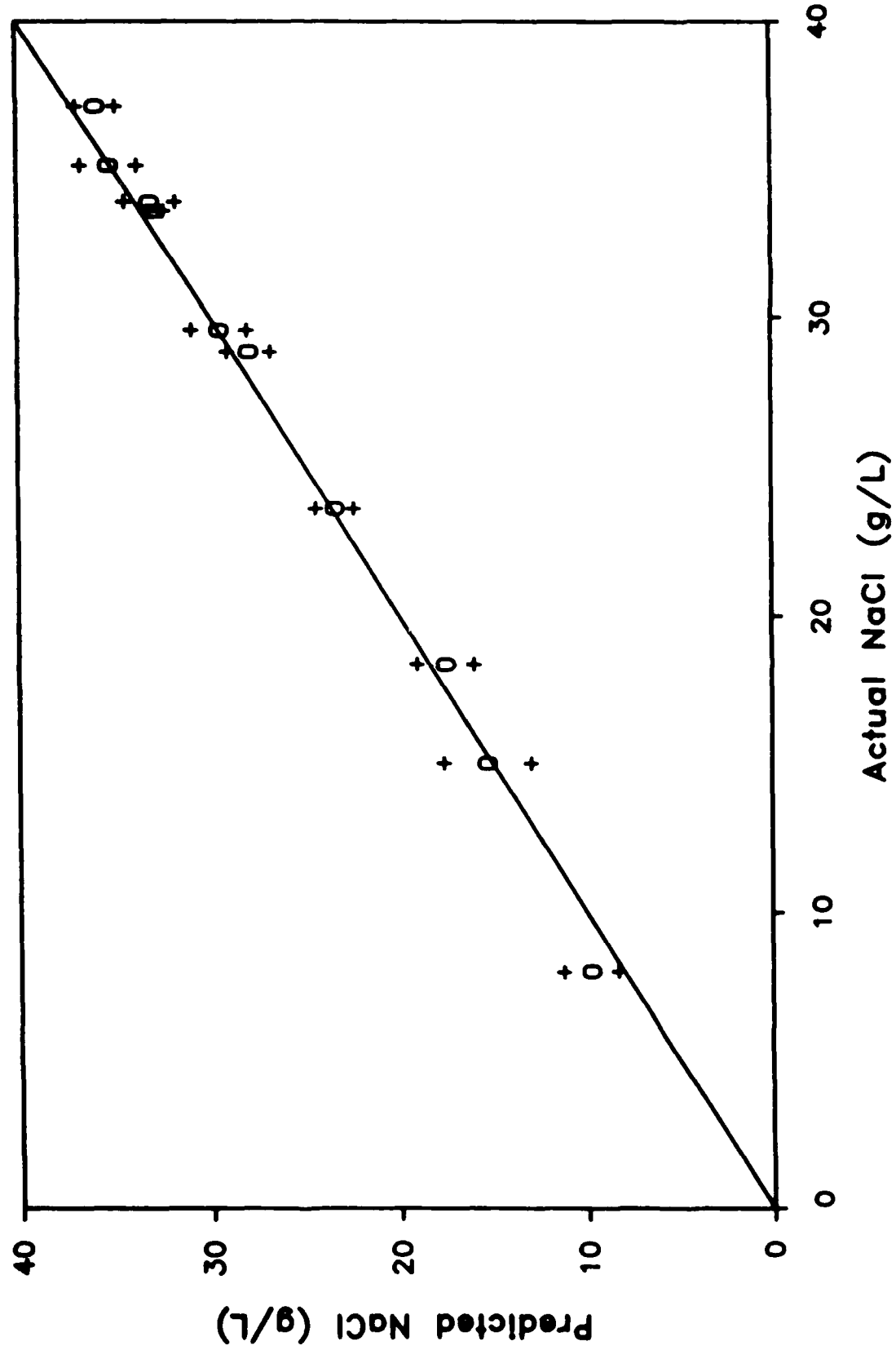

SOURCE LIGHT
1 CM
GLASS SLIDE
SAMPLE
COVER SLIP
SCREW
REFLECTIVE CONE
POLISHED INSERT
MAIN BODY

Fig. 1

Fig. 2



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